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(6-Acetoxy-2-acetylphenyl-$\kappa^2 C^1,O^1$)tetracarbonylmanganese(I)

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(6-Acetoxy-2-acetylphenyl-κ^2C^1,O^1)-tetracarbonylmanganese(I)

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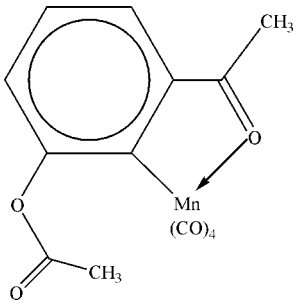
Key indicators: single-crystal X-ray study; T = 168 K; mean σ(C–C) = 0.003 Å; R factor = 0.026; wR factor = 0.073; data-to-parameter ratio = 12.7.

The title compound, $[Mn(C_{10}H_9O_3)(CO)_4]$, is formed by orthomanganation of 3′-acetoxyacetophenone at the sterically crowded *ortho* site. The atoms of the benzene and the cyclometallated rings are coplanar to within <0.018 Å, and there are no significant intramolecular interactions between the $Mn(CO)_4$ group and the adjacent acetoxy group.

Related literature

The preparation and structures of related orthomanganated aryl ketones have been reviewed (Main & Nicholson, 1994). Preference in cyclometallation reactions for the more sterically crowded isomer for other 3′-substituted acetophenones has been observed (Cooney *et al.*, 1988, 2001; Liebeskind *et al.*, 1989).



Experimental

Crystal data

$[Mn(C_{10}H_9O_3)(CO)_4]$
M_r = 344.15
Triclinic, $P\overline{1}$
a = 9.306 (2) Å
b = 9.635 (2) Å
c = 9.954 (2) Å
α = 68.594 (3)°
β = 67.663 (3)°
γ = 68.422 (3)°
V = 740.9 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.92 mm^{-1}
T = 168 (2) K
0.72 × 0.65 × 0.15 mm

Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1998)
T_{min} = 0.711, T_{max} = 0.870
9684 measured reflections
2988 independent reflections
2730 reflections with $I > 2\sigma(I)$
R_{int} = 0.015

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.073
S = 1.02
2988 reflections
235 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.41 e Å^{-3}

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The authors thank Dr Jan Wikaira, University of Canterbury, for collection of X-ray intensity data.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2041).

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supplementary materials

Acta Cryst. (2007). E**63**, m2655 [**doi:10.1107/S1600536807047605**]

(6-Acetoxy-2-acetylphenyl-κ^2C^1,O^1)tetracarbonylmanganese(I)

V. D. Fester, L. Main and B. K. Nicholson

Comment

(2-Acetyl-κO^1-6-acetoxyphenyl- κC^1)tetracarbonylmanganese(I) is formed by orthomanganation of 3'-acetoxyacetophenone at the sterically crowded *ortho* site. The atoms of the phenyl and the cyclometallated rings are coplanar to within <0.018 Å, and there are no significant intramolecular interactions between the $Mn(CO)_4$ group and the adjacent acetoxy one. The Mn1—C12 distance *trans* to O1 (1.8046 (18) Å) is shorter than the Mn1—C11 distance *trans* to C1 (1.8367 (19) Å), while the two Mn—CO distances *trans* to each other are the longest (av. 1.857 (2) Å). The Mn1—C1 distance is significantly shorter than the Mn1—O1 distance (2.0445 (15) and 2.0548 (11) Å respectively) contrary to the trend expected purely on covalent radii. These conform to the pattern found for other orthomanganated arenes (Main and Nicholson, 1994).

Experimental

The title compound was prepared by reaction of $PhCH_2Mn(CO)_5$ with 3'-acetoxyacetophenone in refluxing heptane, under the usual conditions (Main and Nicholson, 1994). The structure was determined to confirm that cyclometallation had occurred at the sterically crowded 2'-position, rather than the alternative 6'-position, and to detect any residual interactions with the adjacent acetoxy group which might have directed this preference.

Refinement

All H-atoms were located as the highest peaks in a penultimate difference map and were refined with isotropic temperature factors.

Figures

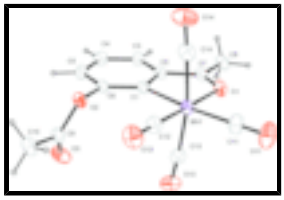

Fig. 1. Structure of (2-Acetyl-κO^1-6-acetoxyphenyl- κC^1)tetracarbonylmanganese(I), with ellipsoids drawn at the 30% probability level.

(6-Acetoxy-2-acetylphenyl-κ^2C^1,O^1)tetracarbonylmanganese(I)

Crystal data

$[Mn(C_{10}H_9O_3)(CO)_4]$	$Z = 2$
$M_r = 344.15$	$F_{000} = 348$
Triclinic, $P\overline{1}$	$D_x = 1.543$ Mg m^{-3}

Hall symbol: -P 1	Mo $K\alpha$ radiation λ = 0.71073 Å
a = 9.306 (2) Å	Cell parameters from 3920 reflections
b = 9.635 (2) Å	θ = 2–26º
c = 9.954 (2) Å	μ = 0.92 mm^{-1}
α = 68.594 (3)º	T = 168 (2) K
β = 67.663 (3)º	Block, yellow
γ = 68.422 (3)º	0.72 × 0.65 × 0.15 mm
V = 740.9 (3) Å^3	

Data collection

Bruker SMART CCD diffractometer	2988 independent reflections
Radiation source: fine-focus sealed tube	2730 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.015
T = 168(2) K	θ_{max} = 26.4º
ω scans	θ_{min} = 2.3º
Absorption correction: multi-scan (SADABS; Sheldrick, 1998)	h = −11→11
T_{min} = 0.711, T_{max} = 0.870	k = −12→11
9684 measured reflections	l = −12→12

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.026	All H-atom parameters refined
$wR(F^2)$ = 0.073	$w = 1/[\sigma^2(F_o^2) + (0.0452P)^2 + 0.1914P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.02	$(\Delta/\sigma)_{max}$ = 0.004
2988 reflections	$\Delta\rho_{max}$ = 0.26 e Å^{-3}
235 parameters	$\Delta\rho_{min}$ = −0.41 e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Mn1	0.15624 (3)	0.30950 (3)	0.24687 (2)	0.03251 (9)
C1	0.37221 (17)	0.14695 (17)	0.24738 (15)	0.0287 (3)
C2	0.46885 (18)	0.18432 (17)	0.30330 (16)	0.0311 (3)
C3	0.6217 (2)	0.09150 (19)	0.31439 (19)	0.0380 (3)
C4	0.6832 (2)	−0.0424 (2)	0.2682 (2)	0.0428 (4)
C5	0.5919 (2)	−0.08368 (19)	0.21356 (19)	0.0389 (3)
C6	0.44005 (18)	0.00979 (17)	0.20521 (16)	0.0314 (3)
C7	0.3934 (2)	0.32656 (18)	0.35101 (16)	0.0337 (3)
C8	0.4716 (3)	0.3870 (2)	0.4155 (2)	0.0425 (4)

C9	0.29739 (19)	−0.15989 (18)	0.22594 (19)	0.0378 (3)
C10	0.2255 (3)	−0.2011 (2)	0.1395 (3)	0.0512 (5)
C11	−0.0262 (2)	0.4716 (2)	0.2641 (2)	0.0509 (4)
C12	0.0719 (2)	0.2290 (2)	0.1657 (2)	0.0415 (4)
C13	0.08616 (19)	0.1809 (2)	0.43689 (19)	0.0395 (4)
C14	0.2643 (2)	0.4043 (2)	0.0558 (2)	0.0470 (4)
O1	0.25602 (14)	0.39925 (12)	0.33756 (13)	0.0383 (3)
O2	0.35525 (14)	−0.03417 (12)	0.14249 (12)	0.0359 (2)
O3	0.30441 (17)	−0.22465 (16)	0.35196 (16)	0.0559 (4)
O11	−0.1391 (2)	0.5708 (2)	0.2727 (2)	0.0809 (5)
O12	0.01425 (17)	0.18291 (17)	0.11287 (17)	0.0599 (4)
O13	0.05411 (16)	0.09520 (18)	0.55063 (15)	0.0572 (4)
O14	0.3357 (2)	0.4562 (2)	−0.06173 (17)	0.0813 (5)
H3	0.679 (2)	0.117 (2)	0.353 (2)	0.046 (5)*
H4	0.788 (2)	−0.112 (2)	0.276 (2)	0.048 (5)*
H5	0.629 (2)	−0.178 (2)	0.182 (2)	0.044 (5)*
H81	0.574 (3)	0.399 (3)	0.353 (3)	0.075 (8)*
H82	0.489 (3)	0.321 (3)	0.506 (3)	0.063 (6)*
H83	0.406 (3)	0.481 (3)	0.435 (2)	0.059 (6)*
H101	0.304 (3)	−0.215 (3)	0.049 (3)	0.081 (8)*
H102	0.143 (3)	−0.120 (3)	0.113 (3)	0.072 (7)*
H103	0.185 (3)	−0.288 (4)	0.196 (3)	0.093 (9)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.03310 (14)	0.02938 (14)	0.03785 (15)	−0.00427 (9)	−0.01615 (10)	−0.00960 (10)
C1	0.0313 (7)	0.0291 (7)	0.0266 (7)	−0.0100 (6)	−0.0102 (6)	−0.0042 (5)
C2	0.0357 (7)	0.0310 (7)	0.0297 (7)	−0.0133 (6)	−0.0121 (6)	−0.0039 (6)
C3	0.0358 (8)	0.0409 (9)	0.0417 (8)	−0.0121 (7)	−0.0175 (7)	−0.0069 (7)
C4	0.0341 (8)	0.0444 (9)	0.0480 (9)	−0.0038 (7)	−0.0168 (7)	−0.0115 (8)
C5	0.0402 (8)	0.0337 (8)	0.0406 (8)	−0.0032 (7)	−0.0123 (7)	−0.0129 (7)
C6	0.0374 (8)	0.0307 (7)	0.0289 (7)	−0.0109 (6)	−0.0115 (6)	−0.0068 (6)
C7	0.0448 (8)	0.0304 (7)	0.0302 (7)	−0.0155 (6)	−0.0148 (6)	−0.0030 (6)
C8	0.0582 (11)	0.0383 (9)	0.0444 (10)	−0.0193 (8)	−0.0241 (9)	−0.0089 (8)
C9	0.0356 (8)	0.0287 (7)	0.0500 (10)	−0.0049 (6)	−0.0148 (7)	−0.0124 (7)
C10	0.0623 (12)	0.0427 (10)	0.0631 (13)	−0.0209 (10)	−0.0232 (11)	−0.0170 (9)
C11	0.0477 (10)	0.0448 (10)	0.0624 (12)	0.0007 (8)	−0.0264 (9)	−0.0182 (9)
C12	0.0398 (8)	0.0392 (9)	0.0482 (9)	−0.0061 (7)	−0.0203 (7)	−0.0105 (7)
C13	0.0323 (8)	0.0479 (10)	0.0430 (9)	−0.0094 (7)	−0.0142 (7)	−0.0147 (8)
C14	0.0565 (10)	0.0435 (10)	0.0458 (10)	−0.0138 (8)	−0.0259 (9)	−0.0045 (8)
O1	0.0462 (6)	0.0299 (5)	0.0451 (6)	−0.0062 (5)	−0.0207 (5)	−0.0128 (5)
O2	0.0471 (6)	0.0323 (6)	0.0362 (6)	−0.0136 (5)	−0.0170 (5)	−0.0091 (4)
O3	0.0630 (8)	0.0504 (8)	0.0587 (8)	−0.0268 (7)	−0.0330 (7)	0.0092 (6)
O11	0.0606 (9)	0.0622 (10)	0.1086 (14)	0.0228 (8)	−0.0392 (9)	−0.0332 (10)
O12	0.0597 (8)	0.0649 (9)	0.0777 (10)	−0.0146 (7)	−0.0405 (8)	−0.0235 (8)
O13	0.0491 (7)	0.0742 (10)	0.0447 (7)	−0.0256 (7)	−0.0133 (6)	−0.0023 (7)
O14	0.0975 (13)	0.0914 (13)	0.0457 (9)	−0.0431 (11)	−0.0189 (8)	0.0090 (8)

Geometric parameters (Å, °)

Mn1—C12	1.8046 (18)	C6—O2	1.4161 (18)
Mn1—C11	1.8367 (19)	C7—O1	1.243 (2)
Mn1—C14	1.849 (2)	C7—C8	1.490 (2)
Mn1—C13	1.8665 (18)	C8—H83	0.93 (2)
Mn1—C1	2.0443 (15)	C8—H82	0.93 (2)
Mn1—O1	2.0548 (11)	C8—H81	0.94 (3)
C1—C6	1.382 (2)	C9—O3	1.195 (2)
C1—C2	1.419 (2)	C9—O2	1.3611 (19)
C2—C3	1.395 (2)	C9—C10	1.493 (2)
C2—C7	1.453 (2)	C10—H101	0.94 (3)
C3—C4	1.376 (2)	C10—H102	0.91 (3)
C3—H3	0.90 (2)	C10—H103	0.94 (3)
C4—C5	1.391 (2)	C11—O11	1.131 (2)
C4—H4	0.97 (2)	C12—O12	1.150 (2)
C5—C6	1.383 (2)	C13—O13	1.138 (2)
C5—H5	0.97 (2)	C14—O14	1.133 (2)
C12—Mn1—C11	90.40 (8)	C4—C5—H5	122.5 (11)
C12—Mn1—C14	89.72 (8)	C1—C6—C5	123.10 (14)
C11—Mn1—C14	95.64 (9)	C1—C6—O2	119.06 (13)
C12—Mn1—C13	90.80 (8)	C5—C6—O2	117.74 (14)
C11—Mn1—C13	96.13 (8)	O1—C7—C2	117.28 (13)
C14—Mn1—C13	168.21 (8)	O1—C7—C8	119.36 (15)
C12—Mn1—C1	100.08 (7)	C2—C7—C8	123.35 (15)
C11—Mn1—C1	169.49 (7)	C7—C8—H83	110.0 (14)
C14—Mn1—C1	85.22 (7)	C7—C8—H82	112.0 (14)
C13—Mn1—C1	83.09 (6)	H83—C8—H82	106.7 (19)
C12—Mn1—O1	179.05 (6)	C7—C8—H81	112.6 (15)
C11—Mn1—O1	90.46 (7)	H83—C8—H81	110 (2)
C14—Mn1—O1	89.80 (7)	H82—C8—H81	105 (2)
C13—Mn1—O1	89.51 (6)	O3—C9—O2	122.64 (15)
C1—Mn1—O1	79.06 (5)	O3—C9—C10	126.36 (16)
C6—C1—C2	115.00 (13)	O2—C9—C10	111.00 (15)
C6—C1—Mn1	132.64 (11)	C9—C10—H102	110.0 (16)
C2—C1—Mn1	112.36 (11)	C9—C10—H103	111.9 (17)
C3—C2—C1	123.14 (14)	H102—C10—H103	108 (2)
C3—C2—C7	122.76 (14)	C9—C10—H101	108.0 (16)
C1—C2—C7	114.09 (13)	H102—C10—H101	106 (2)
C4—C3—C2	118.92 (15)	H103—C10—H101	113 (2)
C4—C3—H3	120.1 (13)	O11—C11—Mn1	178.71 (19)
C2—C3—H3	120.9 (13)	O12—C12—Mn1	177.51 (16)
C3—C4—C5	119.73 (15)	O13—C13—Mn1	175.05 (15)
C3—C4—H4	122.1 (12)	O14—C14—Mn1	176.86 (19)
C5—C4—H4	118.1 (12)	C7—O1—Mn1	117.18 (10)
C6—C5—C4	120.10 (15)	C9—O2—C6	117.20 (12)
C6—C5—H5	117.4 (11)		

Fig. 1